Pestic. Sci. 1997, **50**, 53–63

Adsorption, Desorption and Mobility of Four Commonly Used Pesticides in Malaysian Agricultural Soils*

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(Received 2 August 1996; revised version received 10 January 1997; accepted 5 February 1997)

Abstract: Working with Malaysian agricultural soils, high Freundlich adsorption distribution coefficients ($K_{ads(f)}$) were observed for paraquat (28·7 and 1419) and glyphosate (83·8 and 417) and lower values for 2,4-D (0·57 and 5·26) and lindane (2·65 and 14·1) in a sandy loam and a muck soil, respectively. Desorption of 2,4-D and lindane from the muck soil occurred. The adsorption of the pesticides was not affected by temperature (20°C/30°C), pH or addition of the pesticides as a mixture. Leaching of 2,4-D and lindane was evident under a high water influx (200 mm). Comparable results in the leaching of 2,4-D were observed between laboratory studies and a VARLEACH model prediction.

Key words: adsorption; desorption; mobility; 2,4-D, paraquat, lindane; glyphosate; soil; Malaysia

1 INTRODUCTION

Glyphosate, paraquat, 2,4-D and lindane are commonly used in Malaysian agriculture. The herbicides are used for the control of a wide range of broad-leaved weeds and grasses in plantation crops such as rubber, oil palm and cocoa. Paraquat is often used in vegetable and rice agro-ecosystems for weed clearance prior to the start of a new growing season. Usage of glyphosate for this purpose has gained momentum in recent years as a result of a reduction in the price of the herbicide since its patent expired. The popularity of 2,4-D for the control of broadleaf weeds in the rice ecosystem is reflected in the estimated annual expenditure of RM 4 million on the chemical.[1] Lindane has been reported to offer effective control of the main stemborer species, *Chilotraea polychrysa* (Meyr.) and *Tryporyza incertulas* (Walk.) in the cultivation of rice.[2] Adsorption of pesticides by soils is an important process influencing their migratory behaviour in the various compartments of the environment.

Studies on the adsorption, desorption and mobility of pesticides in soils have been conducted previously on 2,4-D,[3–5] lindane,[6–9] paraquat[10–13] and glyphosate.[14–21] Such studies, however, have not been reported for Malaysian soils. Publications on pesticide leaching and mobility in the soil profile of this country are also not available. Data generated from research on these aspects is of major importance in determining the environmental fate of these pesticides and the potential of groundwater contamination in Malaysian agro-environments. The objectives of the present study were to determine the adsorption-desorption characteristics and the mobility of 2,4-D, lindane, paraquat and glyphosate in two Malaysian agricultural soils.

2 MATERIALS AND METHODS

2.1 Adsorption/desorption

2.1.1 *Soils and Pesticides*

Soils, collected from a rice-growing area in Tanjong Karang (Pasir Panjang) and a vegetable-growing area

* Based on a communication presented at the COST ACTION 66 6th International Workshop ‘Pesticides in the Soil and the Environment’ held on 13–15 May 1996 at Stratford on Avon UK.
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Pestic. Sci. 0031-613X/97/$17.50

in the Cameron Highlands (Kea Farm), were air dried and sieved through a 2-mm sieve. They were classified as muck and sandy loam, respectively, through mechanical analysis (Table 1). The cation exchange capacity (CEC) was determined using 1 M ammonium acetate. The method as described by Allison[22] was employed for determining the organic carbon content. The pH of the soils was also recorded.

[*Ring-U*-^{14}C] 2,4-dichlorophenoxyacetic acid, specific activity $6{\cdot}29 \times 10^5$ kBq mmol^{-1}, radiopurity > 98%, [*U*-^{14}C] lindane, specific activity $3{\cdot}40 \times 10^5$ kBq mmol^{-1}, radiopurity > 98% and [*methyl*-^{14}C]-paraquat dichloride, specific activity $3{\cdot}81 \times 10^5$ kBq mmol^{-1}, radiopurity > 98%, were obtained from Sigma Chemical Company, St. Louis, USA. [^{14}C]Glyphosate, specific activity $18{\cdot}9 \times 10^5$ kBq mmol^{-1}, radiopurity 98·6%, was obtained from Amersham International plc, Amersham Place, Little Chalfont, Buckinghamshire, UK.

2.1.2 Experimental procedure

All determinations were performed in triplicate. An equilibration time was determined using 1·0 mg litre^{-1} solutions of 2,4-D (in ethanol), lindane (in acetone), paraquat (in ethanol) and glyphosate (in water) (1·85, 0·148, 5·92 and 0·925 kBq of the ^{14}C-labelled pesticides respectively, mixed with non-labelled analytical grade materials). A period of 4 h was found sufficient for adsorption equilibration, and degradation of the chemical did not occur in this period.

Pesticide solutions (0·1, 0·5, 1·0, 2·0 and 5·0 mg litre^{-1}) were prepared using non-labelled materials and ^{14}C-labelled 2,4-D, lindane, glyphosate and paraquat, in solvents and with radioactivity as described above. Soil (2 g) was shaken with the pesticide solution (10 ml) on an orbital shaker for 4 h. The contents were centrifuged (3000 rev min^{-1} for 30 min) and the supernatant (1 ml) was radioassayed. The experiment was carried out for sandy loam and muck soils.

Desorption studies were performed in a similar manner using the 1·0 mg litre^{-1} pesticide solutions. After radioassay of the supernatant from centrifugation, the remainder of the supernatant was removed and replaced with aqueous calcium chloride (0·01 M; 10 ml) and the tubes were then shaken for a further 4 h. The desorption equilibration time was slightly longer than that (2 h) employed by Wahid and Sethunathan[7] for lindane and by Piccolo *et al.*[21] for glyphosate. This procedure was repeated four times, after which the soil was air dried, homogenised and samples (0·3 g) were radioassayed using a biological oxidiser.

2.1.3 Effects of pH, temperature and use of a pesticide mixture

A solution of the appropriate pesticide (10·0 mg litre^{-1}) was added to the soil sample (2 g) and the pH adjusted to 4·0 or 6·5 using dilute hydrochloric acid or dilute sodium hydroxide solution. The tubes were shaken (30°C; 1500 rev min^{-1}; 4 h), the contents centrifuged (3000 rev min^{-1}; 30 min) and the supernatant was radioassayed as above. The effect of temperature on adsorption was investigated at 20°C and 30°C. The effect on adsorption of using a mixture of the pesticides was studied using solutions containing 2,4-D, lindane, paraquat and glyphosate (each at 10·0 mg litre^{-1} in 0·01 M calcium chloride). [^{14}C]2,4-D (1·85 kBq), supplemented with non-labelled material, was used when the effect on the adsorption of 2,4-D was investigated, with non-labelled lindane, paraquat and glyphosate added to the mixture. Similar solutions containing [^{14}C]lindane (0·148 kBq), [^{14}C]paraquat (5·92 kBq) or [^{14}C]glyphosate (0·925 kBq) with the other components unlabelled, were used.

A statistical analysis of the above experiments was conducted using SPSS for Windows (Statistical Software published by SPSS). An analysis of variance and the Bonferroni (Least Significance) Test were carried out.

2.2 Mobility

2.2.1 Soil column technique

Muck (120 g) and sandy loam (165 g) soils were placed in a glass column comprising two segments (15 cm length × 2·5 cm diameter) held together using clamps to provide a total depth of 25 cm. The column was covered with black polyethylene on the outside. Radio-

TABLE 1
Physicochemical Properties of Soils Used

Soil type	*Coarse sand* (%)	*Fine sand* (%)	*Silt* (%)	*Clay* (%)	*Organic carbon* (%)	*pH*	*CEC*[a] *(meq 100 g*$^{-1}$*)*
Sandy loam (Cameron Highlands)	54·8	31·6	22·5	10·0	1·3	6·7	7·1
Muck (Tanjong Karang)	0·9	3·8	27·5	32·5	30·5	4·7	54·1

[a] CEC: Cation exchange capacity.

labelled pesticides (18·5 kBq), augmented with non-labelled materials, were introduced into the column. Distilled water (98·1 ml) was then passed through the column to simulate 200 mm rainfall. The flow rate was adjusted such that the volume of water used was eluted within 48 h. The leachate was collected at the end of the two-day period. An aliquot (5 ml) of the leachate was radioassayed. The soil from the top 10 cm, middle 10 cm and bottom 5 cm of the two glass segments was air dried, homogenised and three subsamples from each soil layer were combusted and radioassayed. Three replicate columns were used for each of the pesticides investigated.

2.2.1 Modelling

The CALF model[23] as modified by Walker,[24] Walker and Welch[25] and given the name VARLEACH by Walker and Hollis,[26] was used to predict the leaching of the pesticides. The model was run on a personal computer with a 486 processor.

3 RESULTS AND DISCUSSION

3.1 Adsorption/desorption

3.1.1 2,4-D

Adsorption of 2,4-D to both sandy loam ($r^2 = 0{\cdot}92$) and muck ($r^2 = 0{\cdot}93$) soils was found to best fit a Freundlich adsorption isotherm. Freundlich adsorption distribution coefficients ($K_{ads(f)}$) of 0·57 and 5·26 litre kg^{-1} were obtained for the sandy loam (Table 2) and muck soils (Table 3) respectively. The corresponding $1/n$ values were 0·96 and 0·77, respectively.

The results agreed with the results of several studies indicating a Freundlich adsorption isotherm for 2,4-D.[3–5] Different $K_{ads(f)}$ values were reported, however, as

TABLE 2

Adsorption, Desorption and Organic Carbon Distribution Coefficients of Pesticides in the Sandy Loam Soil

	Pesticide			
Parameter (litre kg^{-1})^a	*2,4-D*	*Lindane*	*Paraquat*	*Glyphosate*
$K_{ads(1)}$	0·49 (±0·07)	3·53 (±0·81)	56·4 (±0·71)	133 (±5·2)
$K_{ads(f)}$	0·57 (±0·69)	2·65 (±1·19)	28·7 (±1·2)	83·8 (±1·4)
$1/n$	0·96 (±0·18)	0·85 (±0·11)	0·60 (±0·05)	0·85 (±0·08)
K_{oc}	43·9 (±53·1)	204 (±91·5)	—	—
K_{des1}	2·57 (±0·34)	16·3 (±6·8)	1304 (±210)	103 (±4·3)
K_{des2}	5·34 (±0·47)	33·4 (±4·6)	NA^b	203 (±8·5)
K_{des3}	10·3 (±1·0)	31·04 (±6·7)	NA	200 (±8·1)
K_{des4}	16·9 (±1·4)	39·7 (±7·1)	NA	251 (±32)
r^2	0·92	0·85	0·96	0·98

^{a} Except for $1/n$.
^{b} NA—Not available as desorption did not occur.

TABLE 3

Adsorption, Desorption and Organic Carbon Distribution Coefficients of Pesticides in the Muck Soil

	Pesticide			
Parameter (litre kg^{-1})^a	*2,4-D*	*Lindane*	*Paraquat*	*Glyphosate*
$K_{ads(1)}$	6·95 (±1·72)	14·6 (±3·0)	1693 (±145)	1188 (±252)
$K_{ads(f)}$	5·26 (±1·27)	14·1 (±1·2)	1419 (±2·2)	417 (±1·4)
$1/n$	0·77 (±0·13)	0·97 (±0·08)	1·01 (±0·13)	0·78 (±0·06)
K_{oc}	17·3 (±4·2)	46·2 (±3·8)	—	—
K_{des1}	28·7 (±3·8)	170 (±31)	NA^b	971 (±200)
K_{des2}	48·5 (±4·0)	317 (±113)	NA	4720 (±5·9)
K_{des3}	51·9 (±11·1)	853 (±371)	NA	4716 (±6·2)
K_{des4}	44·6 (±4·0)	1350 (±430)	NA	NA
r^2	0·93	0·98	0·95	0·99

^{a} Except for $1/n$.
^{b} NA—Not available as desorption did not occur.

a result of differences in soil constituents and pH. The observed $K_{ads(f)}$ values of 1·67 and 8·37 litre kg^{-1} (Tables 2 and 3) were higher than those determined by Grove,[3] who reported $K_{ads(f)}$ values ranging from 0·09 to 1·30 litre kg^{-1} for soils with varying amounts of organic matter content (1·77–10·49%). The higher pH of the soils used (5·9 and 7·8) may account for the lower $K_{ads(f)}$ values observed by Grover[3] in view of the lower proportion of 2,4-D in the molecular form. The observed values were also lower than the $K_{ads(f)}$ of 0·09 on a loamy sand reported by Ogram *et al.*[4] the pH of the sand was, however, not specified. A high $K_{ads(f)}$ value of 204 litre kg^{-1} was observed by Susarla *et al.*[5] for a silty loam soil with a pH of 5·8.

The $K_{ads(f)}$ value obtained from the Freundlich equation for the sandy loam (0·57) was slightly higher than that calculated at the 2,4-D solution concentration of 1·0 mg $litre^{-1}$ ($K_{ads(l)}$; 0·49), while the $K_{ads(f)}$ value for the muck soil (5·26) was lower than $K_{ads(l)}$ (6·95). The differences, however, were not significant.

The higher $K_{ads(f)}$ value observed for the muck soil suggests greater adsorption of 2,4-D to that soil, which was attributed mainly to the high organic matter (52·3%) of the soil. Organic matter is an important factor in the adsorption of 2,4-D to soils as a correlation exists between $K_{ads(f)}$ and soil organic matter content.[3] The lower pH of the soil (4·7) may enhance the adsorption process, as a result of the availability of a higher amount of undissociated 2,4-D.[3] The lower $K_{ads(f)}$ observed for the sandy loam was attributed to the low organic matter (2·2%) of the soil.

The high pH (6·7) of the sandy loam soil may contribute to the lower K_{ads} observed. Most of the 2,4-D would have been in the anionic form at this pH[3] and repulsion of 2,4-D anions to the negatively charged soil colloids would be expected. The clay content in the soil (10·0%) had little or no effect on adsorption as 2,4-D has a low adsorption capacity, including negative adsorption for clays.[27]

The $1/n$ values observed for the sandy loam and muck soils were below unity, indicating that the relative adsorption decreased with increasing solution concentration.[28] A similar observation was made by Grover.[3]

K_{oc} values of 43·9 litre kg^{-1} and 17·3 litre kg^{-1} were determined for the sandy loam (Table 2) and muck (Table 3) soils respectively. Lower K_{oc} values ranging from 16·2 to 22·5 litre kg^{-1} obtained from several soils were reported by Hamaker and Thompson,[29] the lower values resulted from the lower adsorption coefficients. Based on the K_{oc} values observed, mobility of 2,4-D in these soils can be classified as very high (K_{oc} 0–50) following the classification of McCall *et al.*[30] for pesticide mobility in soils.

The weak binding of 2,4-D to soils was indicated by its significant desorption from both soils, 20·3% of the sorbed 2,4-D being desorbed from the sandy loam soil after four successive desorption processes (Table 4). A similar desorption pattern was noted for the muck soil, with 20·4% of the adsorbed herbicide being desorbed. This suggests that, although there was preferential affinity of 2,4-D for muck soil, the binding was essentially weak. K_{des} values of 2·6, 5·3, 10·3 and 16·9 litre kg^{-1} were obtained for four successive desorption processes from the sandy loam. This contrasts with the higher values of 28·7, 48·5, 51·9 and 44·6 litre kg^{-1} obtained for the muck soil. The observed K_{des} values were higher than the 0·24 litre kg^{-1} determined by Susarla *et al.*[5] for a sandy loam.

The relative affinity of 2,4-D for the sandy loam and muck soils was reflected in the percentage radioactivity recovered in the soils. A significant amount (50·0%) of [^{14}C]2,4-D was recovered as soil-bound residues in the muck soil while only 5·08% was recovered for the sandy loam.

TABLE 4
Desorption of Pesticides from Soils

Soil type	*Desorption process*	*Amount desorbed (% of applied)*				*LSD*[a]
		2,4-D	*Lindane*	*Paraquat*	*Glyphosate*	
Sandy loam	1	11·15 (±0·12)	10·81 (±0·24)	0·42 (±0·00)	2·29 (±0·02)	3·85
	2	5·02 (±0·03)	4·62 (±0·04)	0·06 (±0·00)	1·29 (±0·02)	0·45
	3	2·58 (±0·02)	4·28 (±0·11)	0·00 (±0·00)	1·19 (±0·02)	0·44
	4	1·54 (±0·00)	3·12 (±0·05)	0·00 (±0·00)	0·74 (±0·00)	0·07
LSD[a]		1·85	3·41	—	0·37	
Muck	1	7·75 (±0·02)	1·78 (±0·01)	0·00 (±0·00)	0·51 (±0·01)	0·45
	2	4·38 (±0·04)	1·49 (±0·02)	0·00 (±0·00)	0·13 (±0·00)	0·69
	3	4·26 (±0·03)	0·52 (±0·02)	0·00 (±0·00)	0·09 (±0·00)	0·33
	4	3·97 (±0·02)	0·26 (±0·01)	0·00 (±0·00)	0·00 (±0·00)	0·04
LSD[a]		0·42	0·42	—	0·19	

[a] LSD: Bonferroni modified least significant difference.

The adsorption of 2,4-D to the sandy loam and muck soils was not significantly ($P = 0{\cdot}05$) affected by pH (4·0 and 6·7) or temperature (20° and 30°C). Similarly Harris and Warren[31] found no apparent effect of temperature on the adsorption of 2,4-D to peat. As pH increases, the amount of 2,4-D in the molecular form decreases, causing reduced adsorption to soil.[3] This was not, however, observed in the pH range of the present study.

There was no significant difference ($P = 0{\cdot}05$) in the adsorption of 2,4-D to the soils in the presence of pesticide mixtures. This may be attributed to different mechanisms of binding of the pesticides to the soils, resulting in little competition for adsorption sites.

3.1.2 *Lindane*

Adsorption of lindane to the sandy loam ($r^2 = 0{\cdot}95$) and muck ($r^2 = 0{\cdot}98$) soils was found to best fit a Freundlich adsorption isotherm; $K_{ads(f)}$ and $K_{ads(l)}$ were comparable for both soils. $K_{ads(f)}$ and $K_{ads(l)}$ values of 2·65 and 3·53 litre kg^{-1} were observed for the sandy loam, and 14·1 and 14·6 for the muck respectively; $1/n$ values for the two soils were 0·85 and 0·97 respectively. The results were consistent with those of Wahid and Sethunathan[7] who observed a Freundlich adsorption isotherm of lindane for four different types of rice-field soils. In the present study, the $K_{ads(f)}$ values observed were comparable to a value of 1·4 litre kg^{-1} for sand reported by Nordmeyer *et al.*[32] and values of 8·91 and 31·62 litre kg^{-1} reported by Wahid and Sethunathan.[7]

The higher $K_{ads(f)}$ values observed for the muck soil were attributed to the high organic matter content of the muck. This observation was similar to those from several studies conducted previously.[6–8] Organic matter has been demonstrated as the most important factor governing the adsorption and desorption of lindane in soil.[7]

K_{oc} values of 204 and 46·2 litre kg^{-1} were determined from the sandy loam and muck soils. Based on these values, mobility of lindane in soils can be classified between very high (K_{oc} 0–50) and medium (K_{oc} 150–500) following the classification of McCall *et al.*[30] for pesticide mobility in soils. The observed value was lower than the K_{oc} of 1081 litre kg^{-1} reported by Kay and Elrick.[6]

Desorption of lindane occurred in both types of soils, though a significantly higher degree of desorption ($P = 0{\cdot}01$) was observed from the sandy loam. A total amount of 22·83% of [^{14}C]lindane was desorbed from the soil after four successive desorption processes, while a low quantity (4·05%) was desorbed from the muck soil. The same phenomenon was noted by Wahid and Sethunathan,[7] who concluded that desorption of lindane in soils decreased with increasing organic matter content.

The affinity of lindane for organic matter was reflected in the high amount of 62·07% recovered as soil-bound residues in the muck soil; the corresponding figure for sandy loam was 9·42%.

The adsorption of lindane to the sandy loam and muck soils was not significantly ($P = 0{\cdot}05$) affected by pH (4·0 to 6·7), temperature (20°C and 30°C) or when applied in the pesticide mixture.

3.1.3 *Paraquat*

Adsorption of paraquat to the sandy loam ($r^2 = 0{\cdot}98$) and muck ($r^2 = 0{\cdot}95$) soils was found to best fit a Freundlich adsorption isotherm in the concentration range of 0·1 to 5·0 mg litre^{-1}. The observation was contrary to several studies which demonstrated that paraquat adsorption to soils followed the linear form of the Langmuir equation.[12,13] In previous studies high concentrations of solute were used and this may account for the different results observed in the present work. Gamar and Mustafa[12] used high concentrations (up to 0·01 M) in their study while Kookana and Alymore[13] used concentrations of 0·005 to 0·05 M. The Langmuir equation is reduced to a Freundlich relation in the case of dilute solutions,[33] such as those used in the present study, and may account for the observed Freundlich-type adsorption. High $K_{ads(f)}$ values of 28·7 and 1419 litre kg^{-1} were observed for the sandy loam (Table 2) and muck (Table 3) soils respectively. These indicate a high adsorption of paraquat to both sandy loam and muck soils, similar to the results of previous studies.[34–36] Paraquat adsorbs easily to predominantly negatively charged soil colloids. The mechanism of adsorption of paraquat involves ionic and charge transfer bonds[33] and the K_{oc} value of the herbicide may therefore not be applicable.

Desorption of paraquat from the muck was not observed, but low desorption was recorded in the sandy loam after the first (0·42%) and second desorption (0·06%) processes. Subsequent desorption processes, however, failed to displace the paraquat cation from either type of soils. The low desorption observed in the sandy loam may have been caused by the calcium chloride used in the experiment. At the high concentration of 750 g litre^{-1}, calcium chloride has been found to cause an immediate elution of 10% of paraquat from a sandy loam.[36] Estimation of K_{des} was not possible in view of the almost negligible desorption.

Biological oxidation of the soils revealed the high amounts of soil-bound paraquat residues of 60·53% and 84·63% in the sandy loam and muck soils, respectively.

Using an aqueous solution of 10 mg litre^{-1}, adsorption of paraquat was not affected by pH (4·0 to 6·7) in either soil ($P = 0{\cdot}05$), confirming the results of Akhavein and Linscott.[37] Temperature (20°C and 30°C) had no effect ($P = 0{\cdot}05$) on paraquat adsorption, confirming the results of previous studies concerning the adsorption of paraquat to soils with high clay or organic matter content.[11,37]

3.1.4 Glyphosate
Adsorption of glyphosate to the sandy loam ($r^2 = 0{\cdot}98$) and muck ($r^2 = 0{\cdot}99$) soils was found to follow a Freundlich adsorption isotherm. $K_{ads(f)}$ and $K_{ads(l)}$ values of 83·8 and 133 litre kg^{-1}, respectively were observed for the sandy loam, while the corresponding values for muck soil were 417 and 1188 litres kg^{-1}. These results were consistent with those of several previous studies demonstrating a Freundlich adsorption isotherm with glyphosate;[15,18,20,21] the $K_{ads(f)}$ values observed in the current investigation were also comparable to those reported in the literature, which range from 8 to 1835·6 litre kg^{-1}.

A high adsorptive capacity of glyphosate to both sandy loam and muck soils was evident from the high $K_{ads(f)}$ values, and agreed with the results of Sprankle *et al.*[14] The adsorption of glyphosate involves ligand exchange and therefore the K_{oc} value, as in the case of paraquat, may not be applicable.

Desorption of glyphosate from both the sandy loam and muck soils was evident (Table 4), although the desorption was significantly higher ($P = 0{\cdot}01$) in the sandy loam than in the muck soil (5·51% compared to 0·73%) Piccolo *et al.*[21] demonstrated a much higher desorption (15–80%) in their study, depending on the soil characteristics. In either case, it was shown that adsorption of glyphosate to soils is not permanent and that leaching through the soil profile may occur.

The adsorption of glyphosate to the soils was not influenced ($P = 0{\cdot}05$) by pH(4·0–6·7), in agreement with Torstensson.[19] McConnell and Hossner,[18] however, found that adsorption of glyphosate to clays generally decreased as the system pH increased and noted that there were exceptions. Glass[20] observed pH-independent adsorption of glyphosate to the clay mineral illite. By contrast, Nicholls and Evans[38] demonstrated that glyphosate adsorption to a sandy loam increased as pH increased from 2·0 to about 4·0; at higher pH, however, adsorption decreased with increasing pH.

Temperature (20 and 30°C) had no effect on the adsorption of glyphosate to the test soils ($P = 0{\cdot}05$), contrary to the findings of Freed *et al.*[39] who reported a pronounced effect of temperature on glyphosate adsorption.

Application in admixture with the other pesticides did not influence the adsorption of glyphosate to the soils ($P = 0{\cdot}05$) under the conditions of the experiment.

3.2 Mobility

3.2.1 Soil thin-layer chromatography (TLC)
R_f values of 0·36 and 0·05 were recorded for 2,4-D on sandy loam and muck soils, respectively (Table 5); there were no differences in the R_f values between top and sub-soils. These values were lower than those reported by Helling and Turner[40] for a sandy loam (1·00), silt loam (0·50) and silty clay loam (0·69). Nevertheless the R_f value demonstrates the mobility of 2,4-D in a sandy loam soil.

The R_f value of lindane for the sandy loam (0·05) was almost identical to that for the muck soil (0·04); again there were no differences in the mobility between top and sub-soils. A soil TLC R_f value for lindane is not cited in the literature, although values for DDT, dieldrin and endrin, which have similar physicochemical properties to lindane, were found to be zero.[41]

An R_f value of 0·04 was observed for paraquat for top and sub-soils of both the sandy loam and muck soil, which is similar to the R_f value of zero reported for silt, silty clay and sandy loams.[40,41] The R_f value correlates well with results published for laboratory and field studies, indicating the non-migratory behaviour of paraquat in soils.[11]

R_f values of 0·05 and 0·02 were observed for glyphosate in the sandy loam and muck soil, respectively (Table 5) and are comparable to the 0·04–0·14 reported by Sprankle *et al.*[14] on a sandy loam. The immobility of glyphosate in soil measured by this technique provides additional evidence for its strong binding to soils.

3.2.2 Soil column studies

3.2.2.1 2,4-D. Leaching of [^{14}C]2,4-D in the sandy loam and muck soil columns amounted to 4·58% and 0·23% respectively (Table 6), corresponding with the results of several studies, indicating the mobility of 2,4-D in sandy and low organic soils.[41,42] By contrast, Bovey[43] indicated little movement of the herbicide in soils and concluded that 2,4-D posed no hazard due to leaching into the subsoil or in groundwater. The detec-

TABLE 5
R_f Values as Determined by Soil TLC

	Sandy loam		Muck	
Pesticide	*Top soil*	*Subsoil*	*Top soil*	*Subsoil*
2,4-D	0·36	0·35	0·05	0·05
Lindane	0·05	0·05	0·04	0·05
Paraquat	0·04	0·04	0·04	0·04
Glyphosate	0·05	0·03	0·02	0·05

TABLE 6
Pesticide Leaching in Soils under a Simulated 200 mm Rainfall

	Radioactivity (% of applied)			
	Leachate		*Soil*	
Pesticide	*Sandy loam*	*Muck*	*Sandy loam*	*Muck*
2,4-D	4·58 (±1·60)	0·23 (±0·07)	80·87 (±8·00)	76·07 (±9·54)
Lindane	1·050 (±0·013)	0·012 (±0·004)	62·85 (±7·87)	70·56 (±10·01)
Paraquat	0·037 (±0·52)	0·006 (±0·014)	53·13 (±8·51)	77·01 (±6·60)
Glyphosate	0·073 (±0·013)	0·044 (±0·001)	69·1 (±12·9)	69·11 (±8·44)

tion of 2,4-D in groundwater in recent years however, provides further evidence of its mobility in soils.[44]

The residues of [^{14}C]2,4-D in the soil columns amounted to 80·87% and 76·07% in the sandy loam and muck soils respectively. A comparison of the results of the laboratory study and model prediction showed a reasonably good agreement in the amounts of radioactivity found in the leachate of both sandy loam and muck soils (Fig. 1). The amount of [^{14}C]2,4-D found in the leachate of the laboratory study was slightly higher than predicted, possibly due to a preferential flow down the sides of the glass column.

The total amount of [^{14}C]2,4-D found in the sandy loam (80·87%) compared reasonably well with the model prediction (84·82). In the muck soil, however, the observed value was higher than the VARLEACH prediction (27·92%), and may be attributed to a slower rate of degradation of 2,4-D in the laboratory study. The soil used in the study was air dried and sieved before placing in the column, and these processes may have resulted in a decrease of soil microbial population and activity.

Thus, reasonable agreement between the results of the column study and the model prediction was observed only in the sandy loam column. Distribution of [^{14}C]-2,4-D residues in the three layers of the soil column were 39·41 (top 10 cm), 29·78 (middle 10 cm) and 11·68% (bottom 5 cm), compared with the predicted values of 44·99, 34·00 and 5·84%.

3.2.2.2 Lindane. The leachates of the sandy loam and muck soil columns contained small amounts of [^{14}C]lindane (1·05% and 0·012% respectively) indicating that leaching of lindane would be possible under

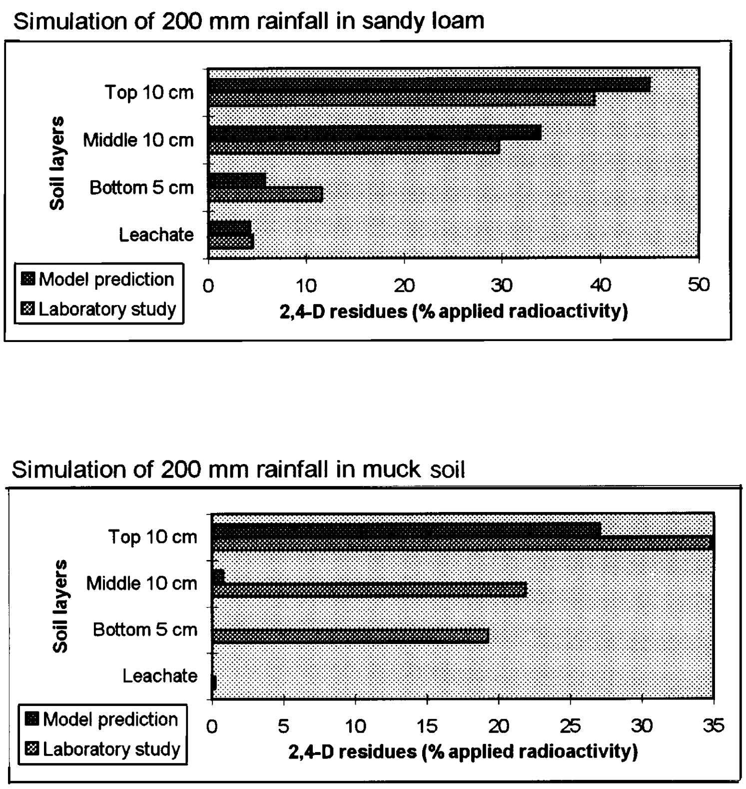


Fig. 1. [^{14}C]2,4-D residues in the leachate and soil layers: a comparison between laboratory studies and a VARLEACH model prediction.

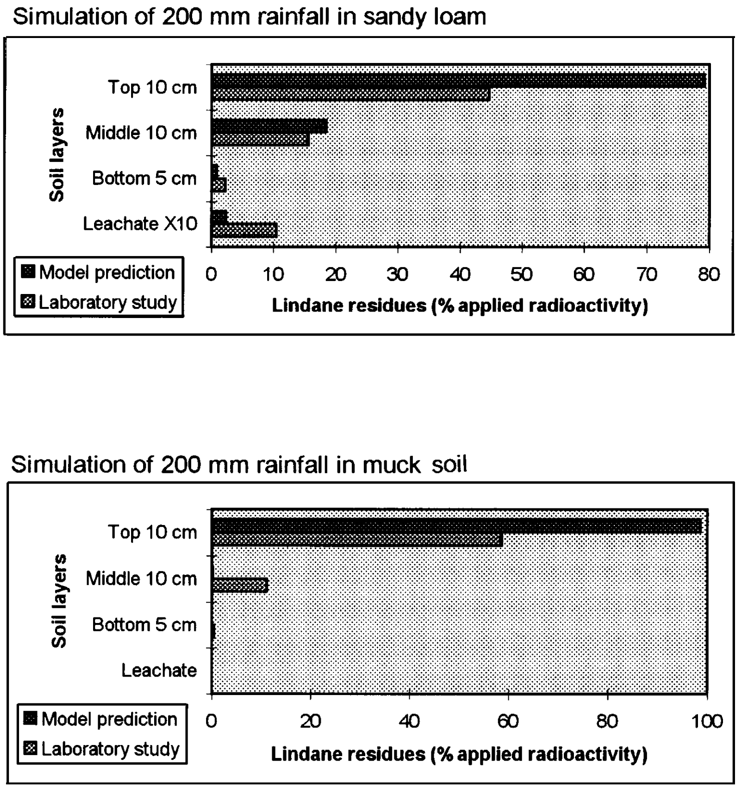


Fig. 2. [^{14}C]Lindane residues in the leachate and soil layers: a comparison between laboratory studies and a VARLEACH model prediction.

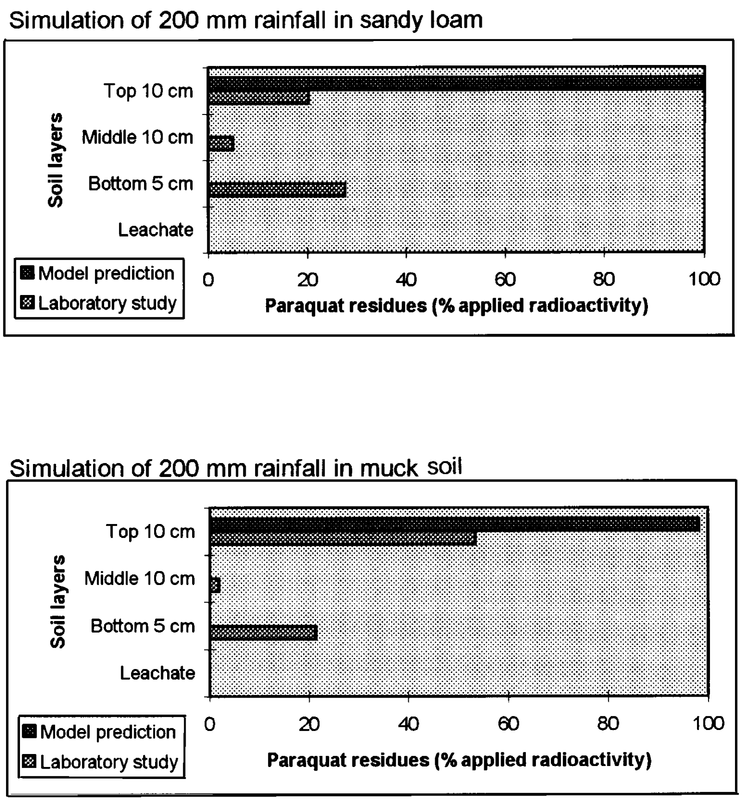
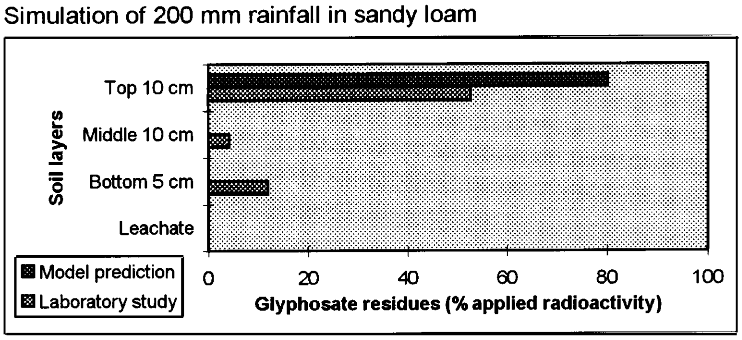


Fig. 3. [^{14}C]Paraquat residues in the leachate and soil layers: a comparison between laboratory studies and a VARLEACH model prediction.



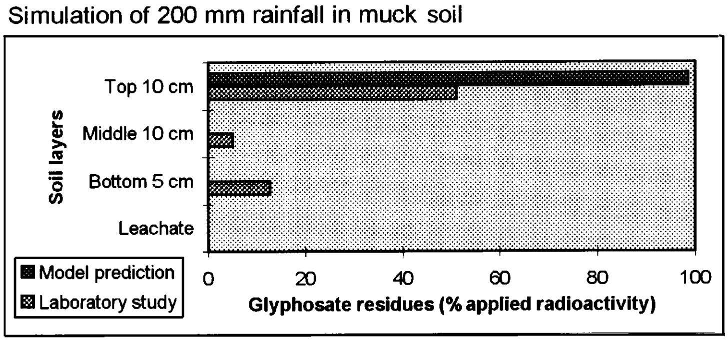


Fig. 4. [^{14}C]Glyphosate residues in the leachate and soil layers: a comparison between laboratory studies and a VARLEACH model prediction.

conditions of heavy rainfall, especially in a sandy loam soil. The results were consistent with those of a field study reported by Adhya *et al.*,[9] who observed the migration of γ-HCH to a lower depth of 30 cm in a soil with sandy clay loam texture. Other studies, however, indicated very little movement of lindane to lower soil layers,[45,46] though the detection of lindane in groundwater[47] strongly supports its mobility in the soil profile.

Results showing the existence of [^{14}C]lindane residues in the leachates (Fig. 2) indicate little difference between the observed (1·05 and 0·012% for sandy loam and muck soils, respectively) and predicted (0·24 and 0·00 for sandy loam and muck, respectively) values.

3.2.2.3 Paraquat. Paraquat leaching was not evident in either sandy loam or muck soil columns, residues in the leachate being virtually absent according to the laboratory study and model prediction (Fig. 3). It has been shown that, following application of paraquat at the agricultural dose rate, its leaching in peat soils is unlikely and no more important than in mineral soils.[11] The distribution of radioactivity in the soil layers, however, was different in the present work. An uneven distribution of [^{14}C]paraquat was observed in the laboratory study, whereas the VARLEACH model predicted limited movement of [^{14}C]paraquat (top 10 cm) in the sandy loam and muck soil columns.

3.2.2.4 Glyphosate. There was little mobility of glyphosate in the muck soil column, as indicated by the low amounts of ^{14}C-radioactivity in the leachate (0·044%). The observation was similar to that reported by Sprankle *et al.*[14] and Roy *et al.*[48] who found limited movement of glyphosate in muck soils.

In the sandy loam soil column, a small quantity of [^{14}C]glyphosate was found in the leachate (0·073%), suggesting slightly greater mobility of the herbicide in this soil. A greater mobility of glyphosate in a sandy soil profile has been observed by Damanakis[17] and, more recently, by Piccolo *et al.*[21] who demonstrated possible leaching of the herbicide to lower soil layers with limited biological activity.

Small amounts of [^{14}C]glyphosate residues were obtained in the leachate of the sandy loam and muck soil columns (0·073 and 0·044% respectively), while the VARLEACH model predicted 0% in both cases (Fig. 4). There were differences in the distribution of ^{14}C-radioactivity in the soil columns. [^{14}C]glyphosate residues were unevenly distributed in the laboratory study, most of the radioactivity being found in the top 10 cm (52·78 and 51·21% for sandy loam and muck soils respectively). Corresponding figures for the middle (10 cm) and bottom (5 cm) segments were 4·31 and 5·12% and 12·02 and 12·78% for sandy loam and muck soils, respectively.

4 CONCLUSIONS

It was observed that adsorption of 2,4-D, lindane, paraquat and glyphosate to the sandy loam and muck soils

followed a Freundlich adsorption isotherm. High $K_{ads(f)}$ values were obtained for paraquat and glyphosate in the test soils, and much more lower values for 2,4-D and lindane; $K_{ads(f)}$ and K_{des} values of the pesticides were higher in the muck soil. Desorption of 2,4-D and lindane was evident from the sandy loam and muck soils but it was not observed for paraquat; desorption of glyphosate occurred from the sandy loam only.

Under the conditions of these experiments, temperature (20°C/30°C), pH (4·0/6·7) and application in admixture with the other pesticides had no effect on the adsorption of 2,4-D, paraquat, lindane and glyphosate to the sandy loam and muck soils. The effect of pesticide mixtures was expected considering the differing adsorption mechanisms and sites for the pesticides.

Soil TLC and column studies showed that only 2,4-D was mobile in the sandy loam and muck soils. Leaching of paraquat and glyphosate was not apparent, while leaching of lindane occurred in the sandy loam. In the case of 2,4-D, comparable results in leaching were observed between laboratory studies and a VARLEACH model prediction.

It was noted that the adsorption-desorption characteristics and leaching behaviour of 2,4-D, lindane, paraquat and glyphosate in the Malaysian soils showed little difference from the results reported in soils from other parts of world.

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